Preparation of Reinforced Soy Protein Adhesive Using Silane Coupling Agent as an Enhancer

Congcong Li,[a] Hongyan Li,[a] Shifeng Zhang,[a,*] and Jianzhang Li [a,*]

Soybean flour (SF)-based adhesives were prepared with either γ-amino, γ-glycidyl, or γ-methacryloyloxy-propyltrimethoxysilane (KH550, KH560, and KH570) silane coupling agents (SCAs) as an enhancer to explore the effect of SCA on the enhancement and mechanisms of the adhesive. Then, the shear adhesion, viscosity, solid content, and morphological properties of the modified SF adhesives were characterized in detail. The cross sections of the cured adhesives were evaluated with a scanning electron microscope (SEM). The results showed that KH560 was the most efficient SCA for improving the water-resistant bonding strength of the modified SF adhesive. With the addition of 3 wt% KH560, the water-resistant bonding strength of the sample was maximized at 0.98 MPa, meeting the requirements for interior plywood. The SEM revealed few holes and cracks, as well as a smooth surface, on the cross section of the cured KH560-modified SF adhesive, indicating that KH560 is a crosslinking agent that could enhance the water-resistant bonding strength of the resulting plywood. In the hot press process, the effects of hot press time and temperature on the water-resistant bonding strength of the adhesives were not significant.

Keywords: Soybean flour adhesive; Silane coupling agent; Water-resistant Bonding Strength

Contact information: MOE Key Laboratory of Wooden Material Science and Application; Beijing Key Laboratory of Wood Science and Engineering; MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Forestry University, Beijing 100083, China;
** Corresponding authors: zhangshifeng2013@126.com; lijianzhang126@126.com*

INTRODUCTION

Petroleum-based adhesives such as urea-formaldehyde, phenol-formaldehyde, and melamine-modified urea-formaldehyde resins are widely used in the wood composites industry (Lei *et al.* 2014). However, concerns have been raised that petroleum-based adhesives will cause increased consumption of petroleum resources, environmental pollution, and public health problems (Zhong *et al.* 2007). There is a growing interest in developing a type of eco-friendly adhesive from renewable resources, such as soybean flour (SF). An adhesive crafted from renewable resources would be considered a viable alternative to petroleum polymers present in the manufacturing of adhesives (Kumar *et al.* 2002; Gui *et al.* 2013).

In recent years, soy-based adhesives have risen to prominence due to their abundance, low cost, and high biodegradability (Chen and Zhang 2004; Gao *et al.* 2012b). Soy-based adhesives were first developed in the early 1930s, but the application of the adhesives was limited because of their poor water resistance and gluing strength (Zhang and Hua 2007; Xu *et al.* 2010). To achieve the desired adhesive properties, it is necessary to modify the protein found in soy based adhesives by alteration of the molecular structure or conformation (Cheng *et al.* 2004). Jang *et al.* (2011) prepared a

new, formaldehyde-free wood adhesive that consists of SF and a recently developed curing agent (CA). The use of sodium hydroxide in SF/CA adhesives can effectively improve the water resistance and dry shear strength of the resulting plywood. Huang and Sun found that by use of soy protein isolates with sodium dodecyl sulfate and sodium dodecylbenzene sulfonate it was possible to achieve higher water resistance and adhesive strength (Huang and Sun 2000). Sun and Bian (1999) found that modification of soy protein with urea improved the adhesion property more so than modification with alkali.

Silane coupling agents (SCAs) can create a chemical bridge due to their bifunctional structures, which can bond with various materials (Fang *et al.* 2014). The SCAs are used to improve the mechanical strength and adhesion ability of composite materials (Plueddemann 1970; Jacob *et al.* 2006; Li *et al.* 2010), as well as to modify resin and surfaces (Tan *et al.* 2006; Fang *et al.* 2014). However, the effects of SCAs on the adhesion property of soy-based adhesives have not been studied. The objective of this study is to investigate the adhesive property and water resistance of three-ply plywood, bonded with soy-based adhesives, and modified by different types and amounts of SCAs.

EXPERIMENTAL

Materials

Soybean flour (SF) (45.2% soy protein, 5% moisture) was purchased from Sanhe Hopeful Group Oil Grain Food Co. Ltd. Poplar veneers (400 mm × 400 mm × 1.6 mm, 8% moisture) were obtained from Wen'an County of Hebei province, China. Quantities of γ-amino, γ-glycidyl, and γ-methacryloyloxy-propyltrimethoxysilane (KH550, KH560, and KH570, respectively) were purchased from Nanjing Xinhuai Scientific Co. Ltd. Other chemicals were analytical grade and obtained from Beijing Chemical Reagents Co. All chemical reactants were of analytical grade.

Methods

Preparation of modified SF adhesives

A representative procedure for preparation of SF adhesives is shown below. The SF (25 g) was mixed with tap water (75 g) and stirred until it became uniform at ambient temperature. Then, different types of SCAs were added separately at different doses to the solution to form a homogeneous system.

Determination of viscosity

The viscosity of the SF adhesive was determined using a DV-II+ viscometer (Brookfield Engineering Laboratories; Middleboro, MA, USA). Spindle S64 was chosen at a rate of 50 rpm at room temperature. The reported values are the average ± standard deviation of three replications.

Solid content measurement

The solid content of the adhesive was tested using the oven-drying method. About 2 g (weight α) of the adhesive was placed into an oven and dried at 100 ± 2 °C until it reached a constant weight (weight β). The solid content was averaged from three parallel samples and calculated as follows:

$$\text{Solid content (\%)} = \frac{\beta(g)}{\alpha(g)} \times 100 \quad (1)$$

Preparation of plywood samples

The adhesive was brushed onto one side of the poplar wood with dimensions of 400 mm × 400 mm (length × width) until the entire area was uniformly covered by the adhesive. Then, three-ply plywood samples were hand-assembled and stored under ambient conditions for 20 min before being hot pressed. The samples were hot-pressed at 130 °C and 1.0 MPa for 6 min. Finally, the plywood was stored at ambient conditions for at least 24 h and cut for evaluation of water resistance.

Water-resistant bonding strength

The plywood's water-resistant bonding strength was determined according to the China National Standard GB/T 9846.3 (2004) for Type II plywood. The plywood was cut into shear specimens (Fig. 1). Eight specimens of each plywood panel were soaked in tap water at 63 ± 2 °C for 3 h and subsequently cooled at room temperature for 10 min. The wet shear strength was tested with a cross head speed of 10.0 mm/min, and the average value ± standard deviation was reported.

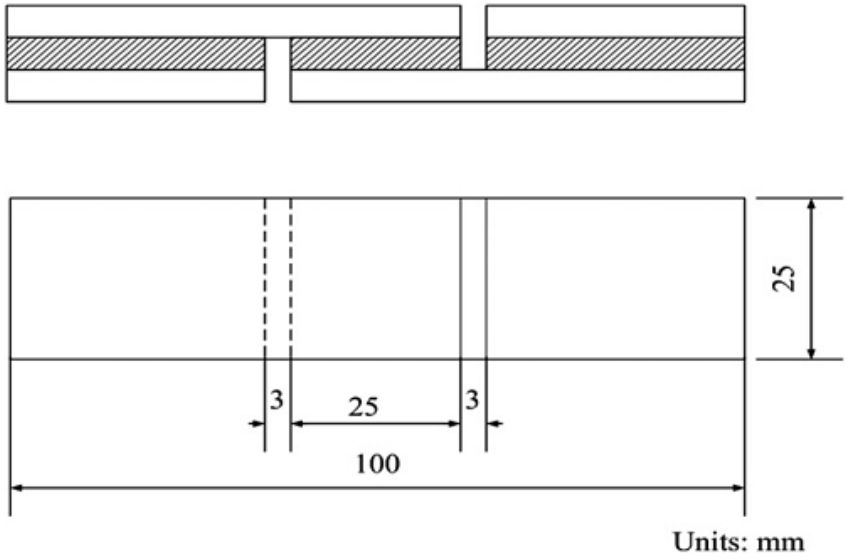

Fig. 1. Lap shear test pieces

Fourier transform infrared (FTIR) spectroscopy

The oven was preheated to 120 °C and then the unmodified and KH560-modified SF adhesives were placed in the oven to a constant weight and then ground into power. The FTIR spectra of the adhesives were recorded on a Nicolet 380 spectrometer (Nicolet Instrument Corporation, Madison, WI) over the range of 400 to 4000 cm^{-1} with a 4 cm^{-1} resolution and 32 scans.

Scanning electron microscopy (SEM)

The samples were dried in the oven at 120 ± 2 °C until each sample reached a constant weight. The cured adhesives were affixed to an aluminum stub with double-sided adhesive tape, and the surface was sputter-coated with gold before observation

under an S-3400N SEM (Hitachi Science System; Ibaraki, Japan) at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Effects of Different Types and Amounts of SCA's on the Water-resistant Bonding Strength of Plywood

Water resistance is an important adhesive property that determines the adhesive bond durability (Gao *et al.* 2011; 2012a). Figure 2 shows the water-resistant bonding strength of plywood that had been bonded by different types of SCA-modified SF adhesives under the same experimental conditions. The results indicated that KH560 was the most reactive and improved the water-resistant bonding strength of the modified SF adhesive. The effectiveness of KH560 in improving water resistance can be attributed to the epoxy group of KH560 that reacted with the amino group of the SF adhesive, which was in accordance with the results of Qin *et al.* (2013). An interpenetrating network (IPN) may potentially be formed in the cured KH570 and SF adhesive system because of the vinyl group of KH570. Therefore, the water-resistant bonding strength of the plywood was improved, which was in accordance with the results of Gao's research (Gao *et al.* 2013). However, the reaction between the siloxane group of KH550 and the hydroxy group of the wood veneer can increase the content of the amino group, because the amino group on the opposite end of KH550 can improve the water absorption (Li *et al.* 2010).

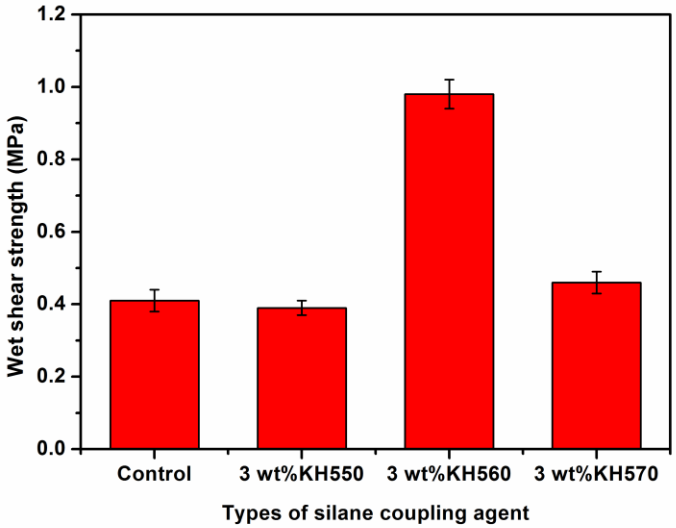

Fig. 2. The effect of different types of SCA-modified SF adhesives on the water-resistant bonding strength of plywood (average ± standard deviation)

Effects of KH560 Dosages on the Solid Content of Modified SF Adhesive

Figure 3 shows the solid content of the adhesives reinforced with different dosages of KH560. Clearly, the solid content of the adhesives increased gradually with the rising dosage of KH560, as depicted in Fig. 3. The solid content increased from 23.3% to 25.9% after addition of 3 wt% KH560, and reached 26.8% with the dosage of 4 wt% KH560. According to reported data, a higher solid content and lower viscosity could lead to a higher wet shear strength (Qin *et al.* 2013).

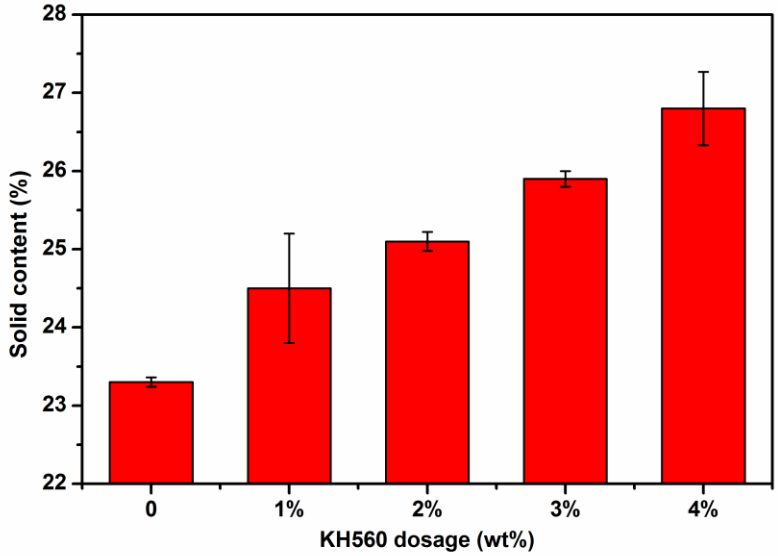

Fig. 3. The effect of KH560 dosage on the solid content of SF adhesives (average ± standard deviation)

Effects of KH560 Dosages on the Viscosity of Modified SF Adhesives

Viscosity is one of the major physical properties governing adhesive behavior on wood veneer. A suitable viscosity provides high flowability on the wood surface (Qi and Sun 2010). The unmodified SF adhesive is so viscous that it cannot sufficiently disperse on the wood veneer surface. The SF adhesive's naturally viscous nature is because of intermolecular interactions, such as electrostatic interaction and disulfide shear between protein molecules (Xu *et al.* 2010). Figure 4 shows the effect of KH560 dosage on the viscosity of SF adhesives.

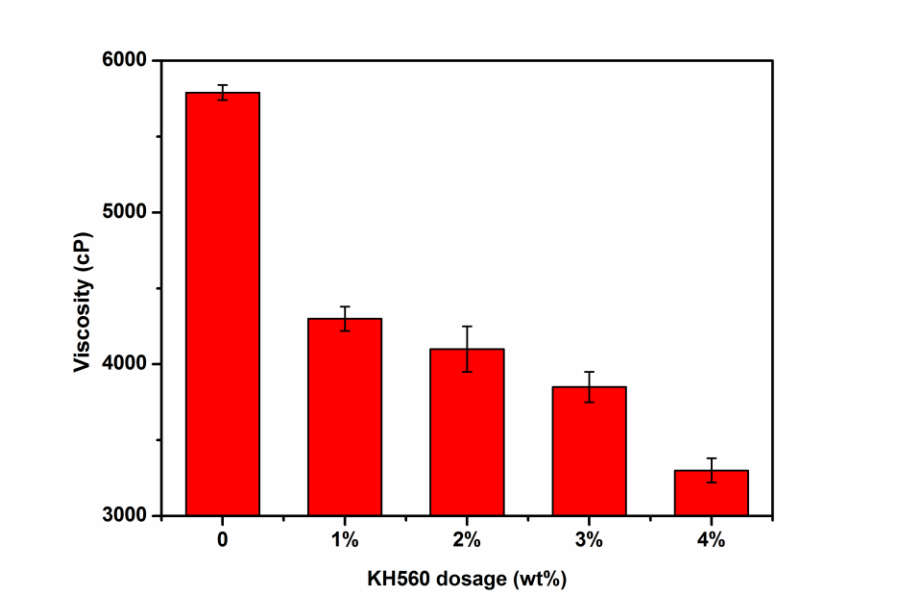

Fig. 4. The effect of KH560 dosage on the viscosity of SF adhesives (average ± standard deviation)

Clearly, the viscosity was lowered with the increasing dosage of KH560. The viscosity was reduced by 26%, from 5790 to 4300 cP, with the addition of 1 wt% KH560. With the increasing dosage, the viscosity consistently decreased, indicating that KH560 could be a direct reducer of viscosity. At the dosage of 4 wt% KH560, the viscosity of modified SF adhesive was reduced by 43% to 3300 cP. The KH560 was used as a plasticizer to weaken the intermolecular forces of the proteins in this system.

Effects of KH560 Dosages on Water-resistant Bonding Strength of Plywood Bonded by Modified SF Adhesive

Figure 5 shows the results of the water-resistant bonding strength of plywood bonded with different dosages of KH560-modified adhesives. The water-resistant bonding strength progressively improved, maximizing at 0.98 MPa with the addition of 3 wt% KH560, but slightly weakened when exposed to increasing amounts of KH560. The water-resistant bonding strength of the modified SF adhesive with the addition of more than 2 wt% KH560 (0.90 MPa) could meet the requirement for interior plywood (≥ 0.70 MPa, or the dashed line in Fig. 5) set by the China National Standard (GB/T 9846.3 2004).

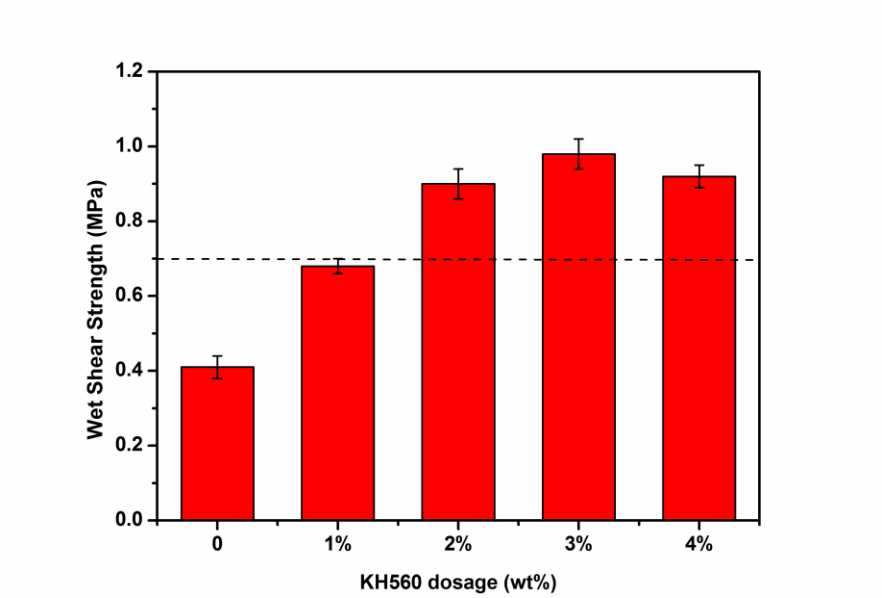

Fig. 5. The effect of KH560 dosage on water-resistant bonding strength of SF adhesives (Type Standard ≥ 0.7 MPa) (average ± standard deviation)

The SF mainly consists of a mixture of soy protein and carbohydrates that are rich with polar functional groups, such as the hydroxyl, amino, and carboxylic acid groups (Wool and Sun 2005). Epoxy has been shown to be an effective cross-linking agent for soy-based adhesives (Lei *et al.* 2014; Qin *et al.* 2013). The KH560 as an SCA that contains the epoxy group and is widely used in caulks and sealants for polysulfide, polyurethanes, epoxy resin adhesives, filled or reinforced with thermosetting resin, glass fiber adhesive and thermoplastic resins filled with inorganic substances or reinforced by glass. The KH560 was used as a crosslinking agent in this study. First, the siloxane bond on one end of KH560 might hydrolyze to a silanol bond (Fig. 6a) and react with the hydroxy group of the wood veneer to form a covalent bond with a heat catalyst. The active epoxy group on the other end of KH560 might react with the amino group present

in the SF adhesive (Fig. 6b). Therefore, with the introduction of KH560, a cross-linked structure was maybe formed to improve the water-resistant bonding strength of the plywood. Figure 6 shows a possible schematic diagram of the whole reaction process.

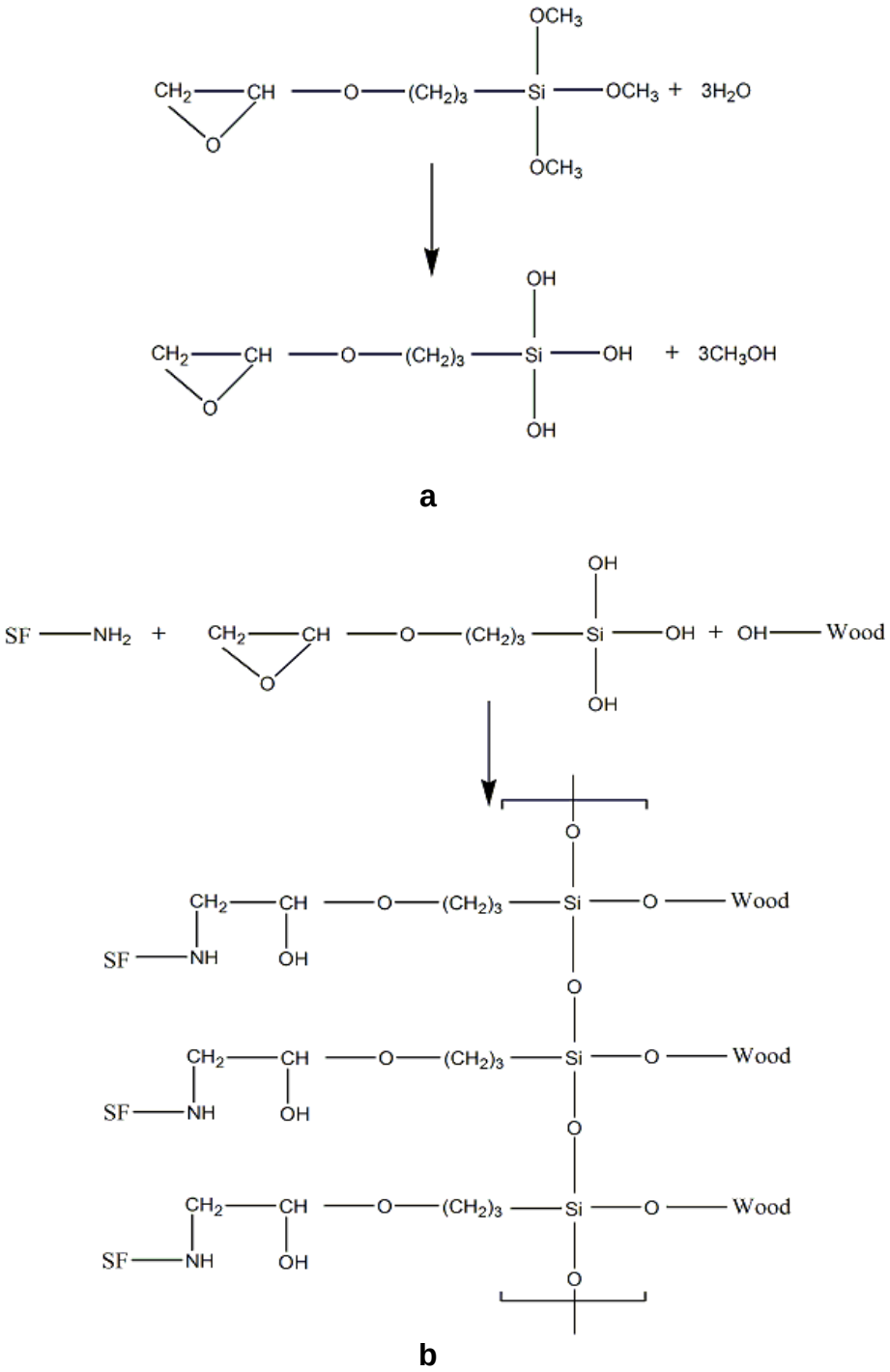

Fig. 6. The structure of KH560 and the possible interactions among KH560, SF, and wood veneer

Effects of KH560 Dosage on the Structure of SF Adhesives

The FTIR spectra of cured SF and KH560-modified SF adhesives are given in Fig. 7. For SF adhesive without addition of KH560 (Fig. 7a), the broad band within 3200 to 3500 cm^{-1} was assigned to the free and bound N-H and O-H groups. The protein characteristic absorption bands at 1656 cm^{-1} (amide I), 1536 cm^{-1} (amide II), and 1237 cm^{-1} (amide III) were related to C=O stretching, N-H bending, C-N stretching, and N-H bending vibration, respectively (Chen and Subirade 2009). The characteristic band of epoxy group of KH560 at 1255, 910, 761 cm^{-1} was not observed in the FTIR spectra, indicating that the crosslinking had occurred between SF and KH560 (Fig. 7b-e). The absorption band at 1194 cm^{-1} resulted from Si-O-CH_3 due to the incomplete hydrolysis of KH560 (Wang *et al*. 2004).

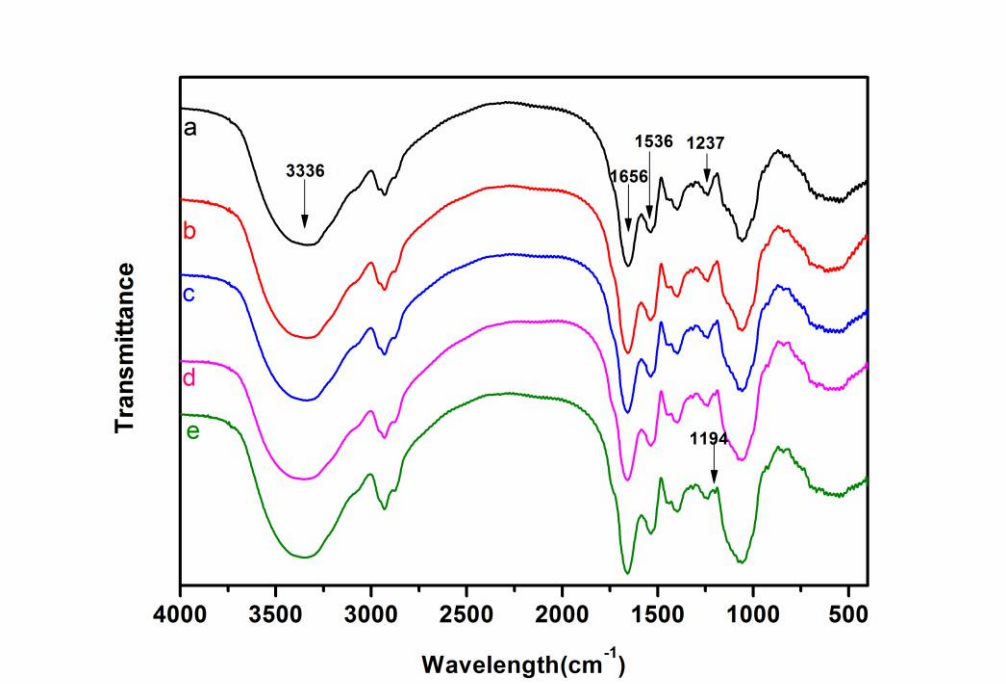

Fig. 7. FTIR spectra of KH560/SF adhesives: (a) SF+0; (b) SF+1; (c) SF+2; (d) SF+3; and (e) SF+4 wt% KH560 adhesive

Cross Sectional Images of the Cured KH560-modified SF Adhesives

Figure 8 shows the cross sections of the cured SF adhesives modified by different amounts of KH560. As depicted in Fig. 8, many holes and cracks were formed on the section of the cured, unmodified adhesive due to the water vaporization of the adhesive during the hot pressing (Fig. 8a). Water or moisture easily intruded into the holes and cracks to break apart the adhesive structure, thus greatly weakening the water resistance capabilities of the unmodified SF adhesive.

With the addition of KH560, fewer holes and cracks were observed on the cross section of the cured adhesive. This phenomenon can be explained through three separate reasons: (1) the main reason was that the crosslinking between KH560 and the SF adhesive led to a more compact structure; (2) KH560, used as a surfactant, also contributed to the formation of the structure; and (3) KH560 reacted with the water in the adhesive system and thus prevented the evaporation of water (Fig. 6).

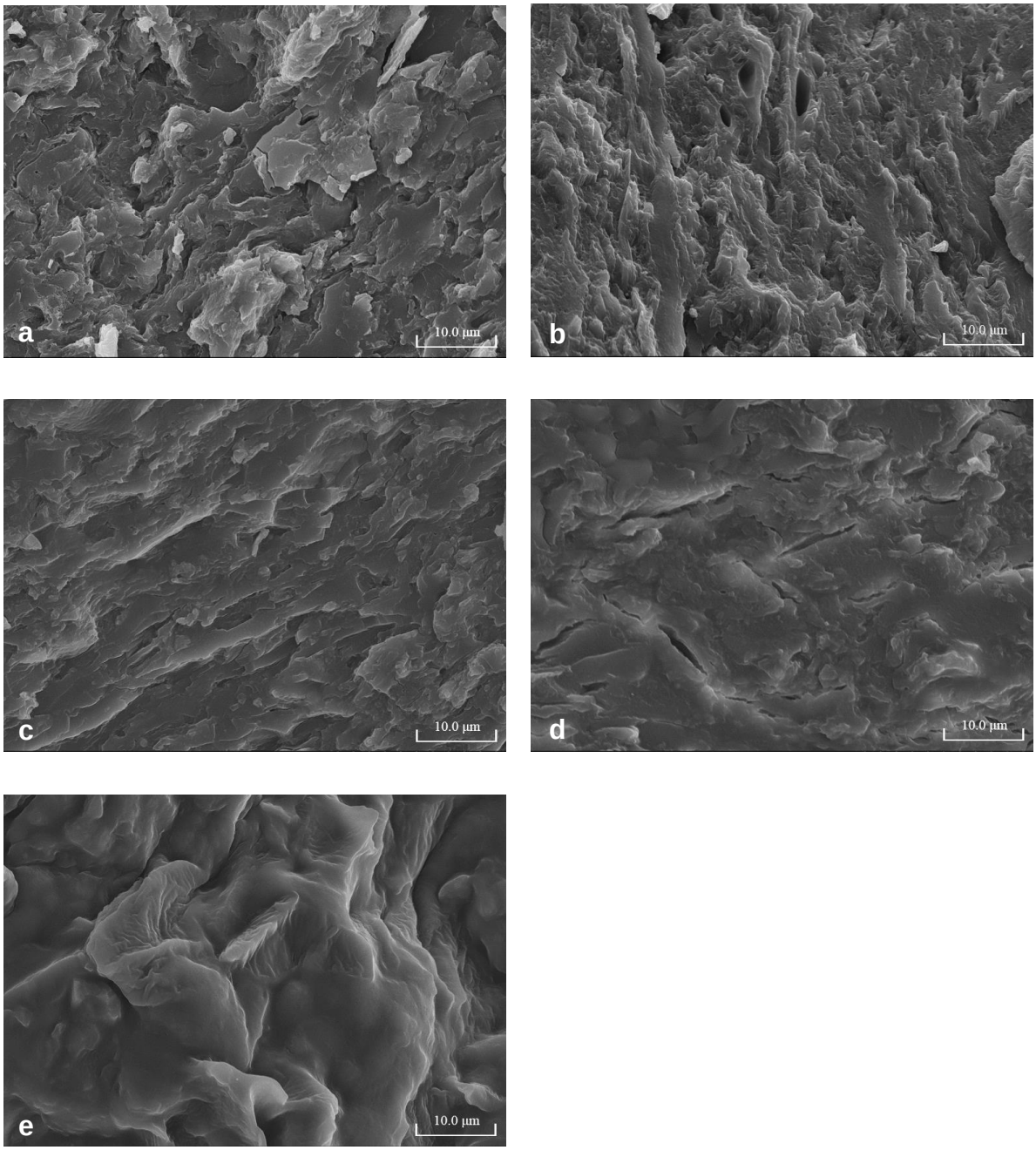

Fig. 8. Cross sections of the cured adhesives in different ratios: (a) SF+0; (b) SF+1; (c) SF+2; (d) SF+3; and (e) SF+4 wt% KH560 adhesive

Effect of Hot Press Temperature on the Water-resistant Bonding Strength of the Plywood Bonded by Modified SF Adhesive

Hot press temperature is a key factor that influences the water resistance of plywood bonded by a SF-based adhesive (Gao *et al.* 2012c). More in depth studies about the effects of hot press temperature on water-resistant bonding strength were conducted to further improve the performance of modified adhesives. The research conducted studied the effects of hot press temperature on the water-resistant bonding strength of the plywood bonded by the modified SF adhesives. The temperature of the hot press used in

the study ranged from 120 to 150 °C, and the samples were subjected to the hot press for a duration of 6 min at a pressure of 1 MPa. The results are shown in Fig. 9. The temperature curve showed that the ideal temperature for maximizing the water-resistant bonding strength was 130 °C (Fig. 9). The water-resistant bonding strength was significantly enhanced, from 0.86 MPa at 120 °C to 0.98 MPa at 130 °C, indicating that the chemical reaction among the KH560, wood, and soy protein was more complete at 130 °C while the pure SF adhesive was 0.40 MPa. However, the water-resistant bonding strength of the plywood bonded with 3 wt% KH560 continually decreased slightly when subjected to incremental increases in temperature, most likely because the higher temperature can cause the partial cleavage of Si-O-Si in the macromolecular structure (Fig. 6). The polyorganosiloxane with Si-O-Si structure that was generated by the cross-linkage of silicon alcohol molecules displayed poor thermostability. At a certain temperature, Si-O-Si could be cracked by oxygen, thus reducing the water-resistant bonding strength (Wang *et al*. 2004).

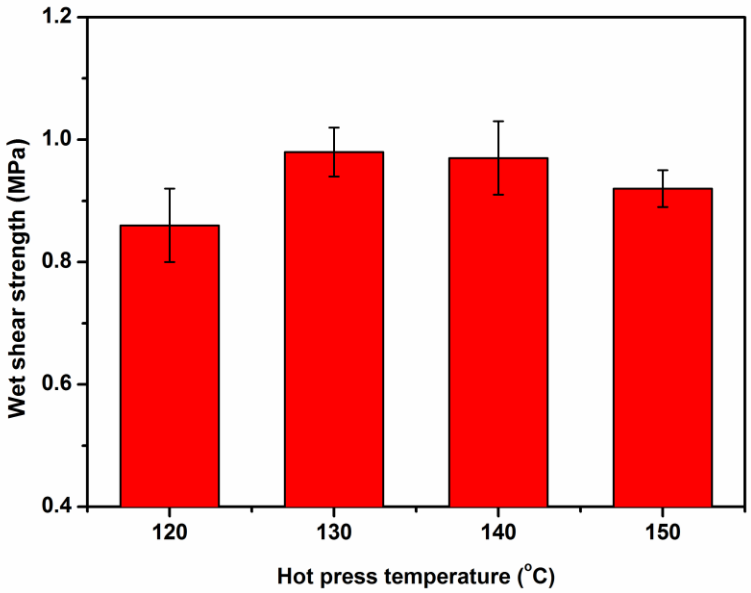

Fig. 9. The effect of hot press temperature on the water-resistant bonding strength of the plywood (average ± standard deviation)

Effect of Hot Press Time on the Water-resistant Bonding Strength of the Plywood Bonded by Modified SF Adhesive

Hot press time is another important parameter that greatly affects the shear adhesion strength of plywood. Figure 10 shows the effects of hot press time on the water-resistant bonding strength of plywood, bonded by modified SF adhesives, at a hot press temperature of 130 °C and pressure of 1 MPa. The water-resistant bonding strength of plywood at hot press times of 6, 7, and 8 min was slightly higher than that at 9 min (Fig. 10). When samples were subjected to the hot press for 9 min, the unstable Si-O-Si bond was partly degraded, accounting for the slight decrease in water resistance.

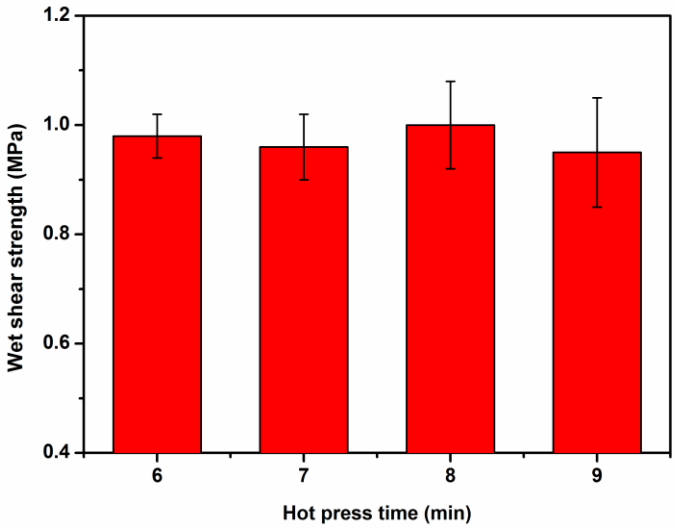

Fig. 10. The effect of hot press time on the water-resistant bonding strength of the plywood (average ± standard deviation)

CONCLUSIONS

1. The KH560 was the most efficient silane coupling agent in terms of improving the water-resistant bonding strength.
2. The wet shear strength of the plywood bonded with KH560-modified SF adhesive improved significantly, from 0.41 to 0.98 MPa after the addition of 3 wt% KH560. The wet shear strength subsequently decreased with further addition of KH560.
3. The viscosity of SF adhesives modified with KH560 was effectively decreased, and the solid content increased, in comparison to the unmodified adhesive.
4. The chemical reaction occurred successfully during the curing process of KH560-modified SF adhesive. A cross-linked structure was possibly formed with the introduction of KH560. The siloxane bond on one end of KH560 might hydrolyze into a silanol bond and then react with the hydroxy group of the wood veneer to form a covalent bond. The active epoxy group on the other end of KH560 might react with the amino group of the SF adhesive. FTIR and SEM also suggested the occurrence of the reaction between KH560 and soy protein.
5. The hot press temperature and time both affected the wet shear strength of the plywood.

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